Pd(II) and Ir(III) catalyzed oxidation of Pharmaceutical drugs (Gabapentin and Paracetamol) by Potassium bromate in acidic medium: A Comparative study

THESIS

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Chemical kinetics deals with the study of the reaction rate and its mechanism. The thermodynamic parameters of any chemical reaction include Gibbs or Helmholtz energy and its relevant equilibrium constant. At equilibrium these parameters are adequate to forecast the suitable product, but have modest application in determining the timescale over which the reactions take place. Consequently thermodynamics may utter that a reaction is spontaneous, but does it happen in 10^{-15} s. The answer to this question lies in the province of chemical kinetics. Chemistry, as Porter(1) rightly points out is "part of statics and part of dynamics" and treated kinetics as later birth and difficult child. Wilhelmy(2) during his first kinetic measurements in 1850 measured the rate of inversion of sucrose and investigated the influence of concentration of sucrose at that moment.

In kinetics, the reactions are classified into two groups:

(a) Homogeneous reactions which come about in one phase.

(b) Heterogeneous reactions where the transformation occurs on the surface of a catalyst or the walls of a container.

Temperature dependence of reaction rates

Temperature has insightful impact on the reaction rate. The consequence of temperature change on the reaction rates can be intimitated in two ways-

1. Temperature coefficient of kinetics of reaction.
2. Arrhenius equation of reaction rates.

Chemical kinetics is of great importance in chemical and pharmaceutical industries. Since the mechanism of a reaction is closely linked with kinetics, and since mechanism is a major topic of inorganic, organic and biological chemistry, the subject of kinetics provides a unifying framework for these conventional branches of chemistry. Catalysis, solid state chemistry and surface chemistry heavily rely on the understanding of the kinetic techniques and analysis. With the evolution of computers and computing techniques, dramatic advances have taken place in quantum mechanical calculations of the potential energy and in theoretical descriptions of rates of reaction. As a result, kinetics is significantly contributing to the rapidly growing subjects such as atmospheric chemistry and environmental studies.

Temperature studies provide important information about the nature of the activated complex as obtained from the values of activation parameters (ΔS^*, ΔG^*, ΔH^* etc.). Making use of these thermodynamic parameters, the proposed mechanism can be justified

Aims and objectives of the present work

The main intent and goal of the proposed investigation may be summarized as follows:-

1. To study the effect of oxidant (Potassium bromate) variation on the rate of reaction in acidic medium.

2. To investigate the impact of catalyst palladium(II) chloride and Iridium(III) chloride, substrate and $Hg(OAc)_2$ on the rate of reaction rate and also elucidate the order with respect to each of them in proposed medium.

3. To study the impact of $[H^+]$, $[Cl^-]$ and ionic strength and also to define its effect on the reaction rate.

4. To study the effect of temperature on the reaction rate.

5. To calculate the thermodynamic activation parameters which are ΔE^*, ΔG^*, ΔS^*, ΔH^* and log A for various reactions.

6. To derive rate law and propose mechanistic steps conforming to the rate on the basis of experimental results.

Materials and methodology

All the reagents used were of highest purity available.

An aqueous solution of substrate, oxidant (potassium bromate), sodium perchlorate and mercuric acetate (E. Merck) were prepared by dissolving the weighed amount of sample in double distilled water. Perchloric acid (60%) of (E. Merck) grade was used as a source of H^+ ions. Sodium perchlorate (E. Merck) was

used to maintain the ionic strength of medium. Reaction stills were blackened from outside to prevent photochemical effect.

The stock solution of potassium bromate (E. Merck) was prepared by dissolving the weighed amount of sample in triple distilled water, standardized iodometrically and stored in dark coloured bottle.

The stock solution of palladium(II) chloride and iridium(III) chloride (Johnson Matthey) was prepared by dissolving the sample in dilute HCl of known strength (0.018N).and was stored in black painted bottle to prevent photochemical decomposition.

Appropriate quantities of solution of mercuric acetate, perchloric acid, KCl, substate and Pd(II)/$IrCl_3$ were placed in a 100 cm^3 jena glass vessel. The requisite amount of double distilled water was added, so that the total volume of the reaction mixture was 50 cm^3 after adding the substrate. The reaction mixture was then placed in a thermostated water bath maintained at desired temperature ± 0.1ºC.

The mixture was allowed to attain the bath temperature and reaction was then initiated by adding the requisite amount of oxidant solution and progress of reaction was followed by determining potassium bromate (oxidant) iodometrically in aliquots withdrawn after regular time intervals, by using starch as an indicator.

Ascertaining the reactive species of potassium bromate in perchloric acid in the present investigation.

It has been reported by earlier workers [3-4] that $KBrO_3$ exists in the

following equilibria in acidic media.

$$BrO_3^- + H^+ \rightleftharpoons HBrO_3 \qquad \text{.....(ii)}$$

$$HBrO_3^- + H^+ \rightleftharpoons H_2Br^+O_3 \qquad \text{.....(iii)}$$

$$H_2Br^+O_3 \rightleftharpoons Br^+O_2 + H_2O \qquad \text{.....(iv)}$$

In acidic solutions Br(v) exists in unprotonated (BrO_3^-) and protonated forms ($HBrO_3$) and ($H_2Br^+O_3/Br^+O_2$) forms. Hence, the oxidation in the present study may be through interaction between the substrate and any one of these oxidant species. All the protonated and unprotonated species, appearing in the kinetic equilibria, may act as reactive species, but one of these species would be predominant in the reaction and may act as real reactive species of $KBrO_3$ in the present investigation. If we assume BrO_3^- as such involved in the reaction, then the rate law derived on the basis mitigate the chances of unprotonated BrO_3^- to be the reactive species, because of the effect of solvent polarity and the acceleration in the rate with increase in [Gabapentin] and [Paracetamol]. Amis et al[5] proposed Br^+O_2 as the oxidizing species in acid bromate oxidation of iodide. Thus, the above species cannot play a dominant role in the reaction. When $H_2Br^+O_3$[6] is taken as reactive species, then it gives rate law which shows second order kinetics with respect to [H^+], which is not observed in the reactions studied, so $H_2Br^+O_3$ is discarded. In acidic solution of

potassium bromate quick formation of $HBrO_3$ has been reported [7].

In case of pharmaceutical drugs BrO_3^- acts as the most reactive species of $KBrO_3$ in the reaction, which gives a rate law capable of explaining all the kinetic observations and other effects.

Ascertaining the reactive species of Palladium(II) chloride in acid medium in the present study.

Palladous chloride is very soluble in HCl and exists as $[PdCl_4]^{2-}$. The existence of different species of palladium chloride, specifically Pd^{2+}, $PdCl^+$, $PdCl_2$, $PdCl_3^-$ and $PdCl_4^{2-}$, has been observed in $HClO_4$ medium depending upon the $[Cl^-]$ / [Pd] ratio. It has been found that species[8] Pd^{++}, $PdOH^+$ and $PdCl^+$ were present when $[Cl^-]$ / [Pd] was up to 0.8; $PdCl^+$ and $PdCl_2$ were present when $[Cl^-]$ / [Pd] was 2.2 – 2.8, and only $PdCl_2$, $PdCl_3^-$ and $PdCl_4^{2-}$ were present[9-10] when $[Cl^-]$ / [Pd] was 4.0 to 4.8. In our experiment $[Cl^-]$ / [Pd] was found to be in the range 2.2 to 2.8, so the reactive species might be $PdCl^+$ and $PdCl_2$. But on the basis of the results obtained Cl^- exists as the following equilibrium in acidic solution of palladium(II) chloride –

$$PdCl^+ + Cl^- \rightleftharpoons [PdCl_2]$$

The positive effect with respect to Cl^- in the present investigation suggests the equilibrium would shift to right. Therefore $[PdCl_2]$ is the reactive species of Palladium(II) chloride in acidic media.

Ascertaining the reactive species of Iridium(III) chloride in perchloric acid medium in the present kinetic study.

It has been reported that Ir(III) and Ir(I) ions are stable species[11] of iridium. Different reactive species of iridium trichloride viz $[IrCl_6]^{3-}$, $[IrCl_5.H_2O]^{2-}$, $[IrCl_4(H_2O)]^-$, $[IrCl_3(H_2O)]$ also exist[12-15]. It has also been reported that in acidic medium Iridium trichloride exist[16] as $[IrCl_6]^{3-}$. Our experimental data indicate that addition of chloride ion has positive effect on the reaction velocity. If addition of chloride ion decreases the reaction velocity then probably the following equilibrium takes place.

$$[IrCl_6]^{3-} + H_2O \rightleftharpoons [IrCl_5H_2O]^{2-} + Cl^-$$

Thus either $[IrCl_6]^{3-}$ or $[IrCl_5.H_2O]^{2-}$ may act as reactive species but chloride ion has positive effect on the rate of reaction in the present investigation therefore $[IrCl_6]^{3-}$ can be safely assumed to be the reactive species.

Role of mercuric acetate in the present study.

The role of mercuric acetate as an oxidant, catalyst and Br^- ions scavenger[10] is well known. In the present investigation, mercuric acetate has been used as scavenger to eliminate Br^- which could have produced Br_2 in the reaction. The bromine thus produced might set another parallel oxidation and create complications in $KBrO_3$ oxidation. Mercuric acetate thus eliminates Br_2 oxidation and ensure that the oxidation proceeds purely through $KBrO_3$.

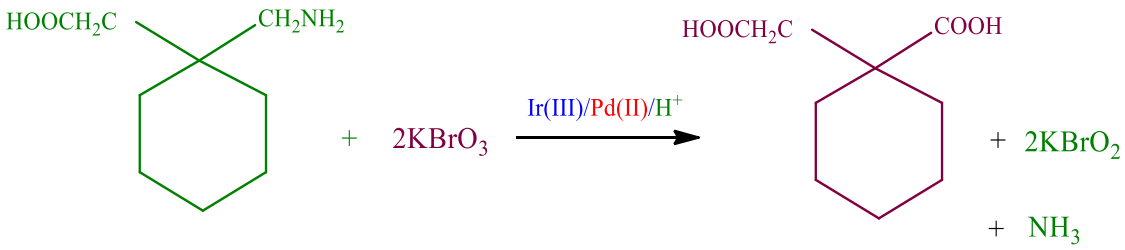
To ascertain the real role of $Hg(OAc)_2$ in addition to Br^- scavenger, several experiments were studied with $Hg(OAc)_2$ in absence of $KBrO_3$ under identical experimental conditions. It has been observed that the reaction does not

proceed in such cases. This rules out the possibility of Hg(II) acting as an oxidant under present conditions of the experiments.

Stoichiometry and product analysis for gabapentin catalyzed oxidation of [Pd(II)/Ir(III)] by potassium bromate in acidic medium.

One mole of substance consumes two moles of potassium bromate in case of Gabapentin. Therefore, accordingly the stoichiometric equations may be given as below.

a) 1-Determination of stoichiometry and product analysis for Gabapentin in acidic medium.



1-amino methyl cyclohexane acetic acid

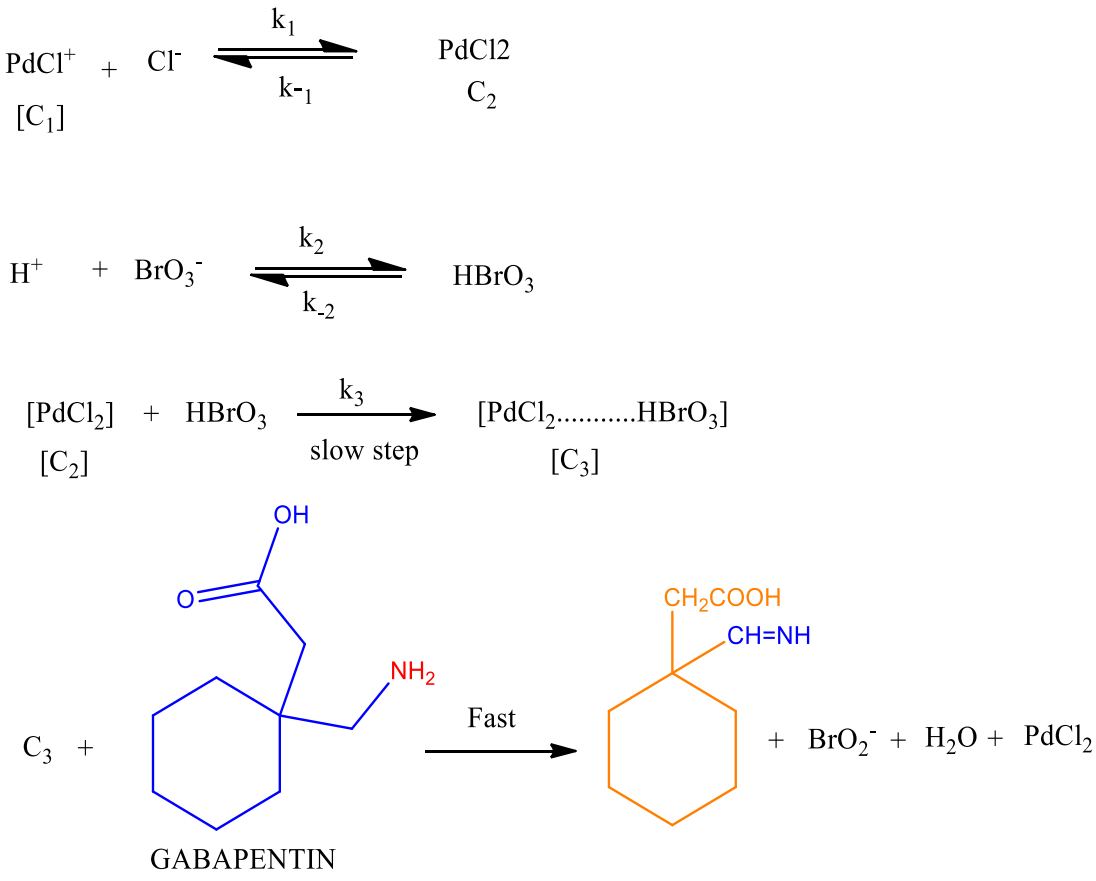
1-carboxy cyclohexane 1-acetic acid

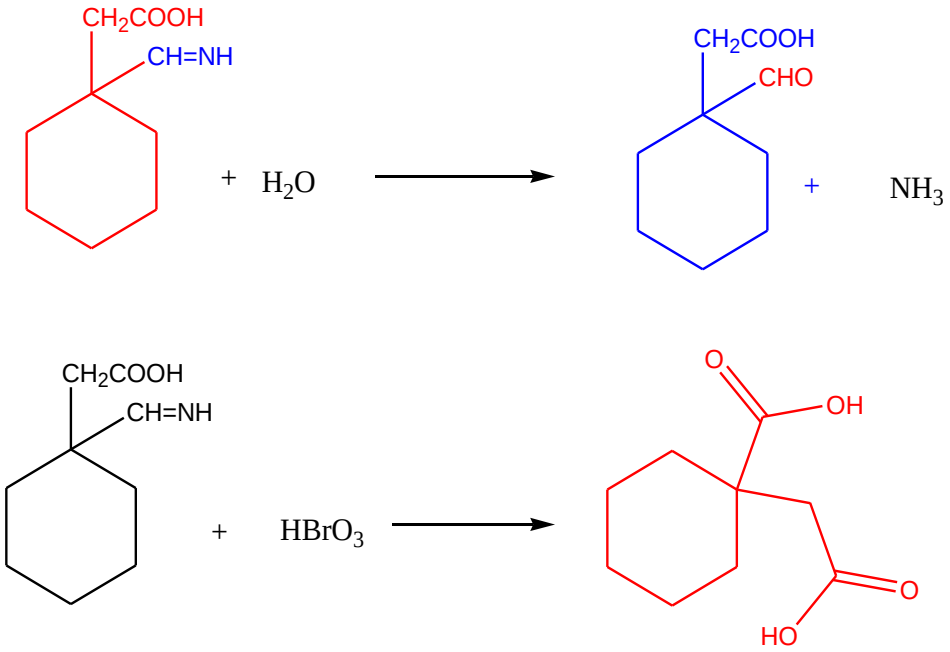
A brief outline of kinetic results obtained in Pd(II) / Ir(III) catalyzed oxidation of Gabapentin by potassium bromate in acidic medium.

The title reaction yielded the following kinetic informations:

1. The reaction follows first order kinetics with respect to oxidant i.e potassium bromate.
2. First order kinetics with respect to catalyst i.e., palladium(II)/Ir(III) chloride.
3. Zero order kinetics with substrate i.e. Gabapentin.
4. Addition of chloride ion to the reaction mixture caused positive change in the reaction velocity.
5. The reaction rate shows first order kinetics with variation in $[H^+]$.
6. Addition of mercuric acetate did not bring about any appreciable change in the reaction rate.
7. Increase in the temperature showed marked effect on the reaction rate.
8. Two moles of Potassium bromate oxidized one mole of substrate (Paracetamol and Gabapentin).

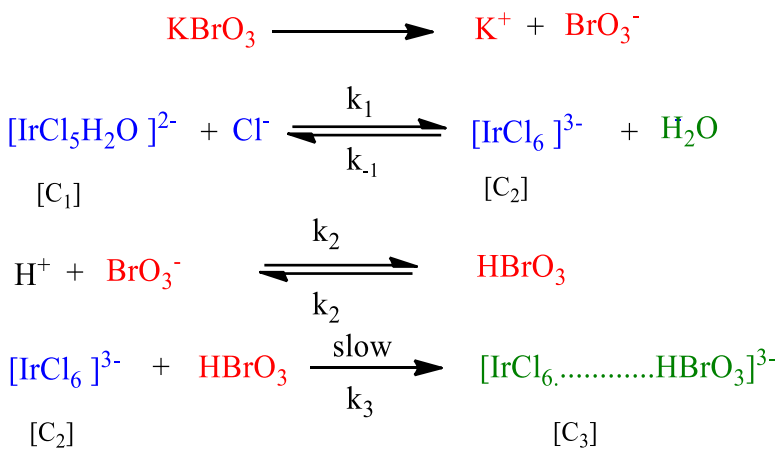
Mechanism of Pd(II) catalyzed oxidation of Gabapentin by Potassium bromate in acidic medium:



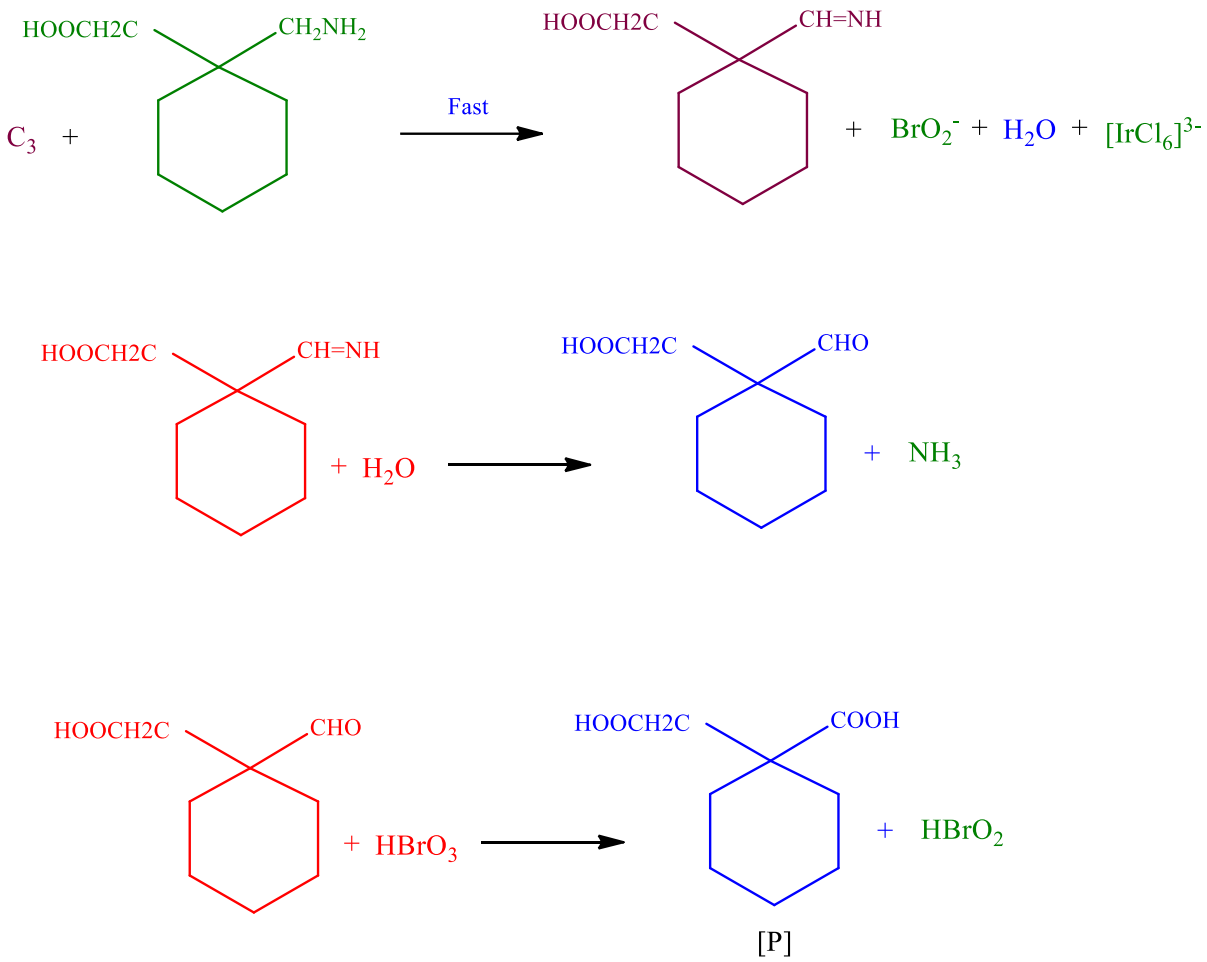


Mechanism of Ir(III) catalyzed oxidation of Gabapentin by Potassium bromate in acidic medium:

[P]



Positive effect with respect to Cl^- in the present investigation suggests that the equilibrium would shift to the right. Therefore $[IrCl_6]^{3-}$ is the active species of Ir(III) chloride in acidic media.



Considering the both proposed mechanism for oxidation of gabapentin by acidic potassium bromate in presence of micro amount of Pd(II) and Ir(III) chloride acting as catalyst and applying the steady state approximation, the rate law may be written as follows.

$$Rate=k_3[C_2]\,[HBrO_3] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$[Pd(II)/Ir(III)]_T=[C_1]+[C_2] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

$$\frac{d[C_1]}{dt} = k_{-1}\,[C_2] - k_1\,[C_1][Cl^-] \quad \ldots\ldots\ldots\ \ldots\ldots \qquad (3)$$

According to steady state approximation $\frac{d[C_1]}{dt} = 0$

$$[C_1] = \frac{k_{-1}\,[C_2]}{k_1\,[Cl^-]} \quad \ldots\ldots\ldots\ldots\ldots \qquad (4)$$

$$[C_1] = \frac{[C_2]}{K_1\,[Cl^-]} \quad \ldots\ldots\ldots\ldots \qquad (5)$$

(*where* $K_1 = k_1/k_{-1}$)

Putting the value of [C_1] from eq. (5) in eq. (2) we get

$$[Pd(II)/Ir(III)]_T = [C_2]\left[\frac{1 + K_1\,[Cl^-]}{K_1\,[Cl^-]}\right] \qquad \ldots\ldots\ldots(6)$$

$$[C_2] = \frac{K_1[Pd(II)/Ir(III)]_{T_1}\,[Cl^-]}{1 + K_1\,[Cl^-]}$$

From step (2)

$$\frac{d[HBrO_3]}{dt} = \frac{k_2\,[H^+][BrO_3^-]}{k_{-2}[HBrO_3]}$$

$$[HBrO_3] = K_2\,[H^+][BrO_3^-]$$

.....(7)

Where $K_2 = \frac{k_2}{k_{-2}}$

Puting the values of [C_2] and [$HBrO_3$] from eq. (6) and (7) in equation (1), we get:

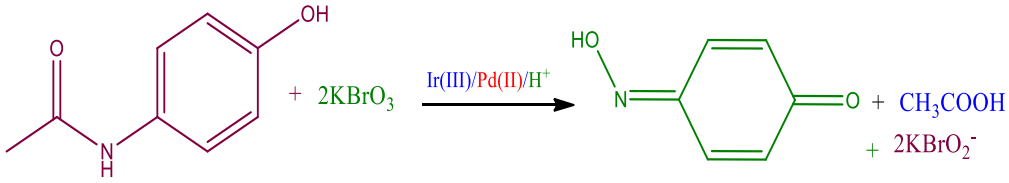
$$Rate = \frac{K_1\,K_2 k_3[Pd(II)/Ir(III)]_T[Cl^-][H^+][BrO_3^-]}{1 + K_1\,[Cl^-]}$$

The rate law derived fully explains first order dependence of the reaction rate on Potassium bromate, Pd(II)/Ir(III) chloride and [$HClO_4$]. zero order dependence of the reaction rate on substrate Gabapentin. The rate law also shows positive effect with respect to potassium chloride.

Stoichiometry and product analysis for Paracetamolcatalyzed oxidation of [Pd(II)/Ir(III)] by potassium bromate in acidic medium.

one mole of substrate consumes two moles of potassium bromate in case of Paracetamol. Therefore accordingly the stoichiometric equations may be given as below.

(b) Determination of stoichiometry and product analysis for Paracetamol in acidic medium.



Paracetamol Quinonoxime

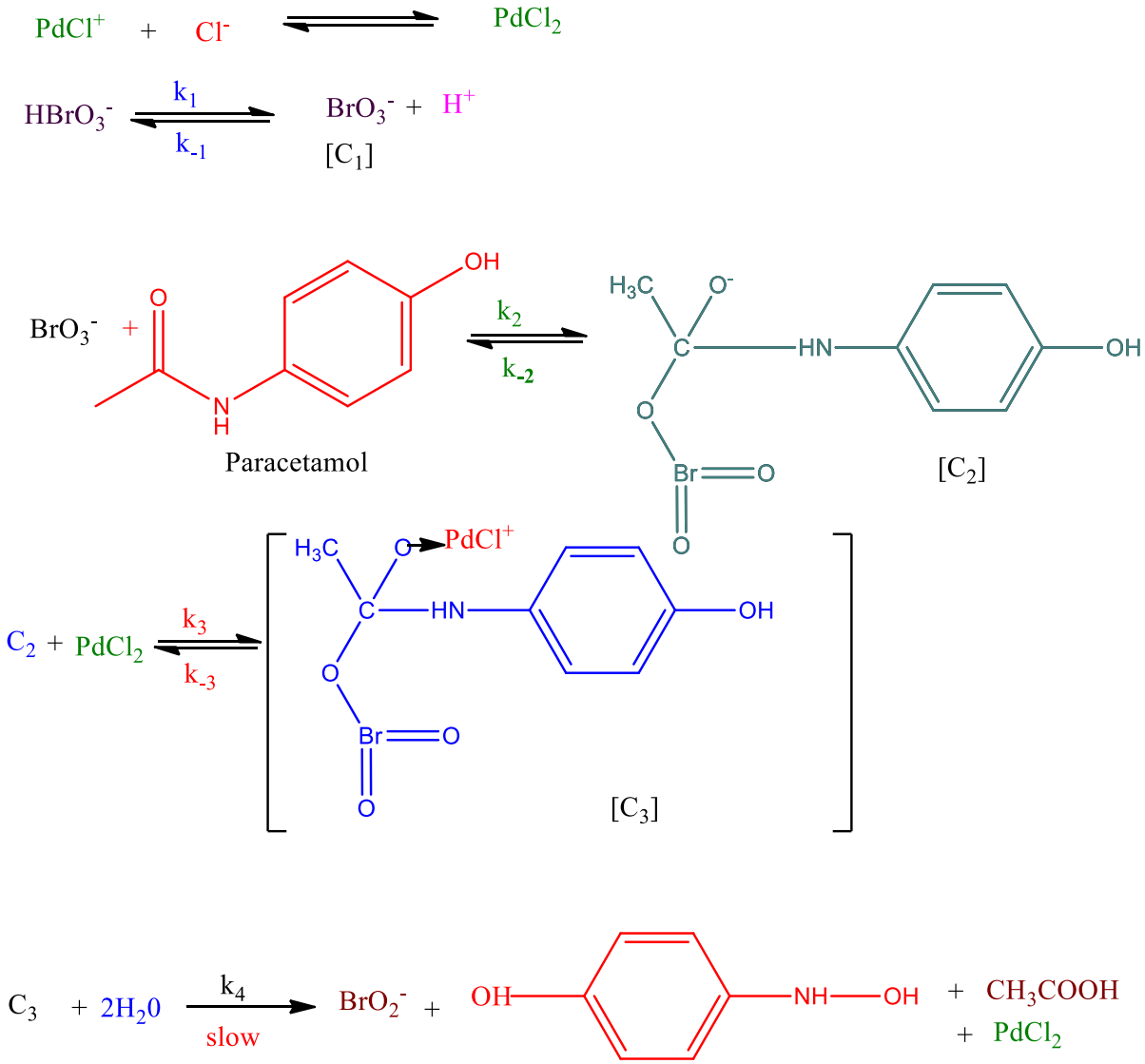
A brief outline of kinetic results obtained in Pd(II)/Ir(III) catalyzed oxidation of Paracetamol in acidic medium.

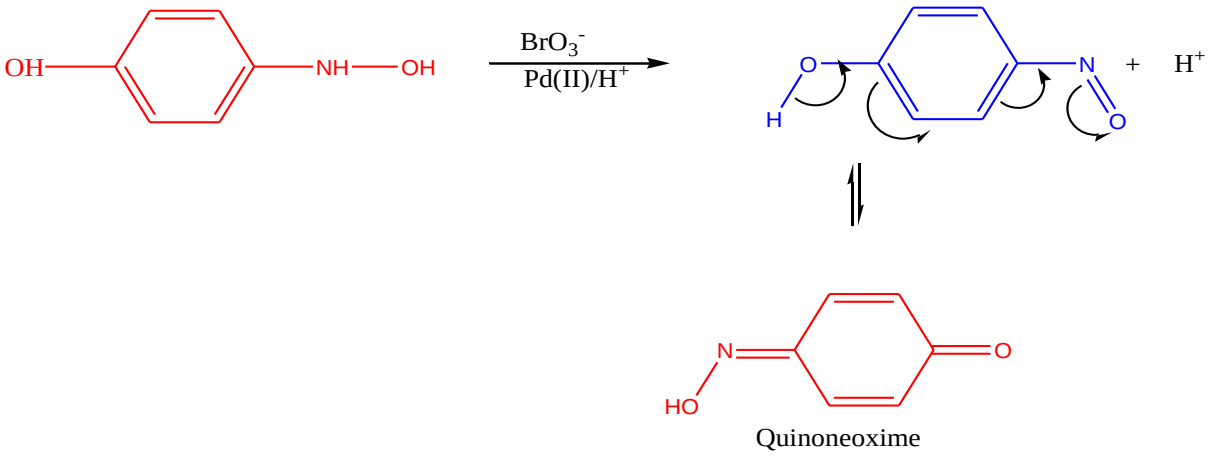
The title reaction yielded the following kinetic informations:-

1. The reaction follows first order kinetics with respect to oxidant i.e. potassium bromate.
2. First order kinetics with respect to catalyst i.e., Pd(II)/Ir(III) chloride.
3. The reaction rate shows negative effect of $[H^+]$.
4. The reaction rate shows positive effect with respect to [substrate] i.e. paracetamol.
5. Addition of chloride ion to the reaction mixture depicts no change in the reaction rate.
6. Addition of mercuric acetate did not influence the rate of reaction.
7. Zero effect of variation of ionic strength of the medium was observed.
8. Increase in the temperature showed marked effect on the rate of reaction.
9. Two mole of Potassium bromate oxidized one mole of substrate (Paracetamol).

Mechanism of Pd(II) catalyzed oxidation of Paracetamol by potassium bromate in acidic medium:

The BrO_3^- species has been reported to act as an oxidising agent in acidic as well as in alkaline medium. Pd(II) chloride has been reported to give a number of possible chloro species dependent on pH of the solution. the following reaction scheme may be suggested.


PdCl+ + Cl- PdCl2
HBrO3- k1 k-1 BrO3- + H+
[C1]
BrO3- +
OH
O
N
H
Paracetamol
k2
k-2
H3C
O-
C
HN
OH
O
Br
O
O
[C2]
C2 + PdCl2
k3
k-3
H3C
O
PdCl+
C
HN
OH
O
Br
O
O
[C3]
C3 + 2H20
k4
slow
BrO2- +
OH
NH
OH
+ CH3COOH
+ PdCl2



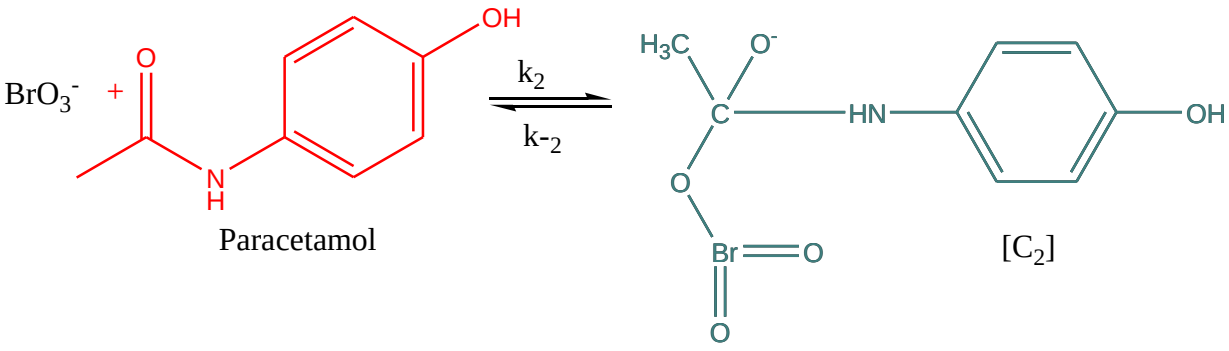
Quinoneoxime

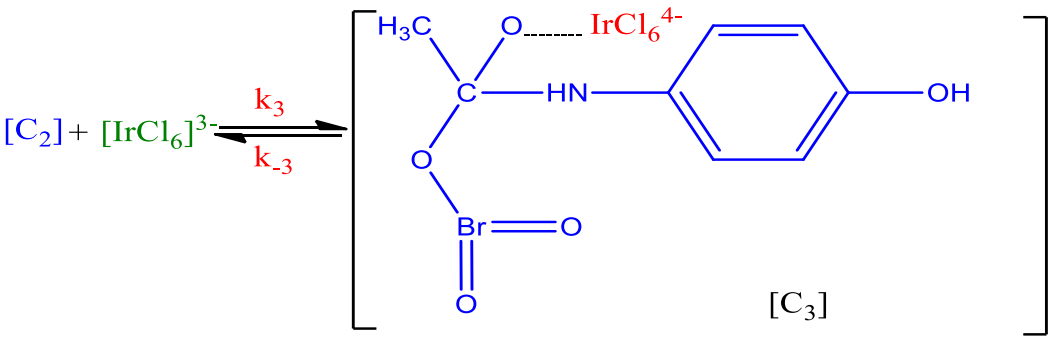
Mechanism of Ir(III) catalyzed oxidation of Paracetamol by Potassium bromate in acidic medium:

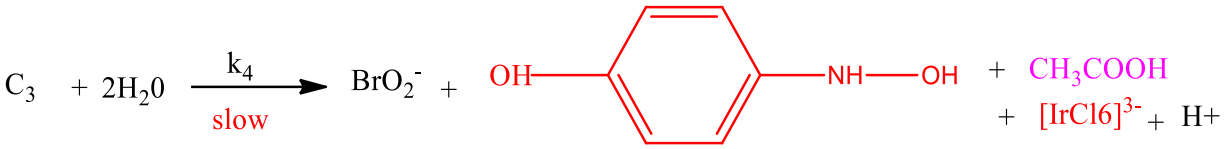
$$[IrCl_5(H_2O)]^{2-} + Cl^- \rightleftharpoons [IrCl_6]^{3-} + H_2O$$

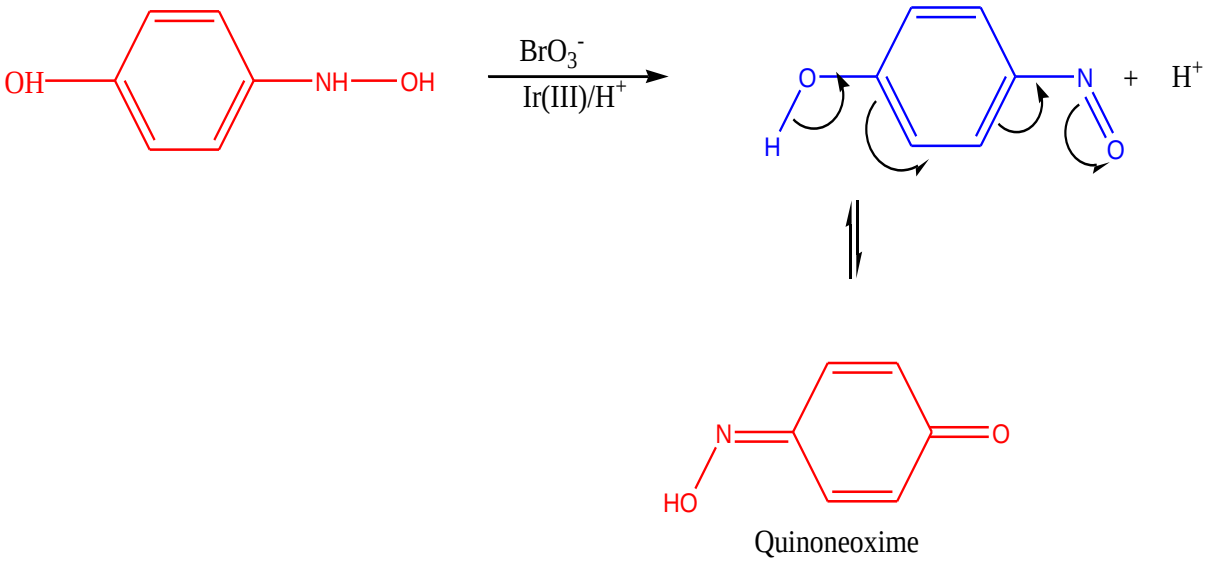
$$HBrO_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} BrO_3^- + H^+$$

$$[C_1]$$


BrO3-
+
O
N
H
OH
Paracetamol
k2
k-2
H3C
O-
C
HN
OH
O
Br
O
O
[C2]


[C2] + [IrCl6]3-
k3
k-3
H3C
O
IrCl6 4-
C
HN
OH
O
Br
O
O
[C3]


C3 + 2H20
k4
slow
BrO2-
+
OH
NH
OH
+ CH3COOH
+ [IrCl6]3- + H+



Quinoneoxime

Considering the both proposed mechanism for oxidation of paracetamol by acidic potassium bromate in presence of micro amount of [Pd(II)] and [Ir(III)] chloride acting as catalyst and applying the steady state approximation, the rate law may be written as equation.

$$\text{Final Rate} = k_4[C_3] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

On the basis of scheme above step (1) we can be obtained in the following

form respectively as-

$$\frac{d[C_3]}{dt} = k_3[C_2]\,[PdCl_2]/\,[IrCl_3] - k_{-3}\,[C_3]$$

$$[C_3] = K_3[C_2]\,[PdCl_2]/[IrCl_3]$$

$$\frac{d[C_2]}{dt} = [k_2][C_1][PA] - k_{-2}[C_2] - k_3[C_2]\,[PdCl_2]/[IrCl_3] + k_{-3}[C_3]$$

Substituting the value of [C_3] we get

$$\frac{d[C_2]}{dt} = k_2\,[C_1]\,[PA]\; - k_{-2}\,[C_2]\; - k_3\,[C_2]\,[PdCl_2\,]/[IrCl_3] + k_{-3}(k_3[C_2]\,[PdCl_2]/[IrCl_3])$$

$$[C_2] = K_2\,[PA]\,[C_1]$$

$$\frac{d[C_1]}{dt} = k_1\,[HBrO_3] - k_{-1}\,[C_1][H^+] - k_2\,[C_1]\,[PA] + k_{-2}\,[C_2]$$

Substituting the value of [C_2] we get

$$\frac{d[C_1]}{dt} = k_1\,[HBrO_3] - k_{-1}\,[C_1][H^+] + \cancel{k_2\,[C_1]\,[PA]} + k_{-2}\,\cancel{\frac{k_2}{k_{-2}}\,[PA]}\,[C_1]$$

$$\mathrm{k}_1[HBrO_3] = \; k_{-1}\,[C_1][H^+]$$

$$[C_1] = K_1 \frac{[HBrO_3]}{[H^+]}$$

$$Rate = \frac{k_1\, k_2\, k_3\, k_4 [PdCl_2]/[IrCl_3]\, [PA][HBrO_3]}{[H^+]} \ldots\ldots\ldots\ldots (2)$$

At any time in the reaction the total concentration of $HBrO_3$ that is $[HBrO_3]_T$ can be expressed as-

$$[HBr0_3]_T = [HBr0_3] + [C_1] + [C_2] + [C_3] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Substitution of the variable of $[C_1]$ $[C_2]$ and $[C_3]$ in equation [3]. Equation [4] is obtained.

$$[HBr0_3]_T = [HBrO_3] + \frac{K_1[HBrO_3]}{[H^+]} + K_2[PA]\frac{K_1[HBrO_3]}{[H^+]} +$$

$$K_3([PdCl_2]/[IrCl_3]K_1K_2[PA]\frac{[HBrO_3]}{[H^+]}$$

$$[HBr0_3]_T = [HBrO_3]\,(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2[PA]}{[H^+]} + \frac{K_1K_2K_3[PdCl_2]/[IrCl_3][PA]}{[H^+]})$$

$$[HBrO_3] = \frac{[HBrO_3]_T\,[H^+]}{[H]^+ + K_1 + K_1K_2[PA] + K_1K_2\, k_3[PdCl_2]/[IrCl_3][PA]} \ldots\ldots\ldots\ldots (4)$$

Substituting the value of $[HBrO_3]$ from eq.(4) in eq.(2) we get

$$\text{Final} \quad Rate = \frac{K_2\, K_3 k_4 [PdCl_2]/[IrCl_3]\,[PA][HBrO_3]_T\, \cancel{[H^+]}}{\cancel{[H^+]}\,\{\,[H^+] + K_1 + K_1\, K_2[PA] + K_1\, K_2\, K_3[PdCl_2]/[IrCl_3]\,[PA]\,\}}$$

The value of $K_1\, K_2\, K_3[PdCl_2]/[IrCl_3]\,[PA]$ is negligible so it can be neglected.

$$\text{Therefore, Final} \quad Rate = \frac{K_1 K_2\, K_3 k_4 [PdCl_2]/[IrCl_3][PA][HBrO_3]_T}{[H^+] + k_1(1 + k_2[PA])}$$

Calculation of the activation parameters

In this section an attempt has been made to calculate the different activation parameters. For this, the reaction has been studied at four different temperatures and with the help of observed rate/rate constant, the energy of activation (E_a), entropy of activation (ΔS^*), enthalpy of activation (ΔH^*), free energy of activation (ΔG^*) and Arrhenius frequency factor (A) have been computed for different reactions. The activation parameter have been calculated with the help of following equations.

(i) $$\frac{\Delta S^*}{4.576} = \log k_r - 10.573 - \log T + \frac{E_a}{4.576T}$$

All values are in calories

(ii) $$\Delta H^* = E_a - RT$$

(iii) $$\Delta G^* = \Delta H^* - T\Delta S^*$$

(iv) $$\log A = \log k_r + \frac{E_a}{2.303RT}$$

The calculated values of various activation parameters for different redox systems are as follows:-

Table 8.0

Values of Activation Parameters for pharmaceutical drugs in Pd(II) and Ir(III) catalyzed oxidation by potassium bromate in acidic medium

Arrhenius Parameters	Pd(II) chloride Gabapentin Paracetamol		Ir(III) chloride Gabapentin Paracetamol	
E_a kJ mol^{-1}	52.42	61.27	66.67	53.33
Log A	10.34	10.79	12.66	10.80
ΔS^*JKmol^{-1}	-56.99	-23.18	-6.51	-42.12

ΔG^* kJ mol^{-1}	70.18	68.42	68.71	66.60
ΔH^* kJ mol^{-1}	52.67	61.27	66.67	53.62

References

1. G. Porter: vol 1, *Pergamon press*, 7, **1967.**
2. L. Wilhelmy: *Pogg. Ann.*, vol 81, 413-499, **1850.**
3. Sanjeev Reddy Ch. and Sundaram E.V: *Tetrahedron.*, vol 45, 2109, **1989.**
4. Edwards J.C: *Chem. Rev.,* vol 50, 455 **1952.**
5. Amis E.S., Indelli A, Nolen G: *J. Am. Chem. Soc.*, vol 82, 3233, **1960.**
6. Beck M.T., Rabai G.Y., Bazsa G.Y: *Int. J. Chem. Kinet.*, vol 13, **1981.**
7. C.S. Reddy, E.V. Sundaram: *J. Indian Chem. Soc.*, vol 62, 209, **1985**.
8. Droll Block & Fernelius W.C: *Phy. Chem.*, vol 61, 1000, **1975**.
9. Neeti Grover, Neelu Kambo & Santosh K. Upadhyay: *Ind. J. of Chem.*, vol 41A, 2482 – 2488, **2000.**
10. Ajaya Kumar Singh, Reena Negi, Bhawana Jain, Yokraj Katre, Surya Prakash Singh: *Ind. Eng. Chem. Res.*, vol 50, 8407 – 8419, **2011.**
11. F.A. Cotton and G. Wilkinson*: Willey Eastern Ltd. New Delhi*., 434, **1976.**
12. G. Gopal Krishna n, B.R. Bajpai, N. Venkatas Subramanian: *Ind. J. Chem.*, vol 19B, 293, **1980.**

13. V. I. Kravtsov and G. M. Petrova; *Russ. J. Inorg. Chem.,* vol 9, 552 **(1964)**
14. I. A. Poulshen and C. S. Garner*: J. Am. Chem. Soc.,* vol 84, 2032 **(1962)**
15. A. J. P. Dominqos, A. M. T. S. Dominqos and J. M. P. Gabral.*: J. Inorg. Nucl. Chem.,* vol 31, 2563 **(1969)**
16. J. C. Chang, C. S. Garner: *Inorg. Chem.,* vol 4, 209 **(1965)**